

Surface Properties of Coal-Oil Agglomerates in the Floc Regime

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1 Introduction

Agglomeration processes bring together fine powders into larger masses in order to improve powder properties. In conventional coal mining procedure, much of the fine coal (typically -100 mesh) is rejected with tailings as it is impractical to recover. Due to the heterogeneous nature of coal, smaller particles tend to be individually richer in ash or carbonaceous matter compared to the overall composition of the coal. This discretization facilitates effective separation. The tailings are handled in water slurry form and in an agglomeration/separation treatment, an immiscible oil phase (usually any liquid hydrocarbon of size C_7 or greater) is added under high-shear mixing conditions to enhance surface wetting. The oil selectively adheres to the carbonaceous surfaces and also acts as a bridging liquid to consolidate several oiled coal particles into an enlarged agglomerate. The ash is excluded and is separated via screening or by selective bubble flotation. [1,2,3] Yield-ash results are shown for the agglomeration flotation of a Pennsylvania coal in Figure 1. [4] The results compare well with other recovery methods.

The agglomerate flotation technique has been known since the turn of the century [5], but to date, there is a considerable gap in understanding of the fundamentals involved. Since the coal-oil agglomerates in this context are a product of an upstream formation process, the material properties of the system are more or less fixed, and work has shown that such properties are favourable for flotation. [6] Flotation performance depends on both hydrodynamic and surface chemical interactions. [7,8]

Thus, it is the objective of this study to investigate the surface properties of a coal-oil agglomerate system to provide a database for subsequent work on their flotation properties.

2 Experimental

The coal selected for this work was a high-grade metallurgical coal provided by the Cape Breton Development Corporation. It contains 2.18% ash by weight (proximate analysis), and hence can be used as is to study its agglomeration properties.

2.1 Agglomerate Preparation

Prior to making any surface property measurements, the procedure for agglomerate preparation had to be established.

Agglomerates were prepared at a 10% pulp density. The coal (density = 1.3 g/cm³) was mixed with distilled water and stirred under vacuum in a baffled flask for about 90 minutes to remove complications arising from the presence of air in the system. [9] After de-airing, a required volume of hexadecane was added and the mixing continued for a further thirty minutes to form the agglomerates. Agglomerates were prepared at hexadecane levels ranging from (based on weight percent of coal) 0.25% to 10.0%.

2.2 Surface Tension Measurements

The surface properties of the agglomerates were determined by the adhesion technique. [10,11]

Briefly, this technique involves measuring the extent of particle adhesion to various solid substrates as a function of the composition (surface tension) of the suspending liquid. A water-methanol system was used, since hexadecane is immiscible across their entire binary composition range. [12] Thus the agglomerate structure is not interfered with. Surface tensions of binary water-methanol mixtures span possible coal and/or oil surface tensions. For cases where the surface tension of the suspending liquid differs from the particle surface tension, adhesion should be a function of the substrate surface tension, γ_{SV} . For the case where $\gamma_{LV} = \gamma_{PV}$ the change in free energy due to particle adhesion is zero. Thus the γ_{LV} where the adhesion is not a function of γ_{SV} will be equal to γ_{PV} .

The adhesion method surface tension measurements were carried out as described in detail by Absolom *et al.* [10,11]

Four different polymer film substrates were used to span the possible surface tensions of the coal-oil system. These polymers were polystyrene, sulfonated polystyrene, polyethylene and polyethyleneterephthalate. The adhering agglomerates on these films were then recorded on video tape through a stereo microscope. Using image analysis, the area percent adhesion was determined. Each experiment was duplicated.

2.3 Particle-size distribution Measurements

The particle-size distributions for the agglomerates were obtained using a Malvern model 2600 laser diffraction particle-size analyser. This instrument measures the largest dimension of the particles as they are instantaneously positioned in the laser path, and determines an average over at least 500 pulses. Several measurements were made at each oil level.

Additionally, the particle-size distributions of agglomerates were determined suspended in a mixture of 95% CH_3OH and 5% H_2O , at several oil levels to verify that the methanol in the suspending liquid did not influence the particle-size distributions.

3 Results

Results were obtained for the surface tension of the agglomerate particles and the particle-size distributions at several oil levels.

3.1 Surface Tension Results

The adhesion method was employed to determine the surface tension of hexadecane-coal agglomerates at several oil levels. The procedure outlined in [10] was used to determine γ_{PV} at each oil level. Figure 2 shows the agglomerate surface tensions versus oil level. The surface tension of the unoiled coal was 62.0 dyne/cm, in agreement with other published results for bituminous coal. [10,13,14] At 10 weight% oil, the agglomerate surface tension closely approximates that of pure hexadecane.

3.2 Particle-Size Distribution Results

Figure 3 shows the agglomerate particle-size distributions for each measured oil level. The mean particle-size of the unagglomerated coal is 33 μm . As one would expect, the mean size increases as more oil is added to the system.

4 Discussion

In light of the dependence of the surface tension and the mean size of the agglomerates on oil level, the corresponding three-phase contact angles and bond volumes were evaluated.

4.1 Determination of the Three-Phase Contact Angle

Measured and tabulated surface tension values were used along with an equation of state approach to determine the three-phase contact angle. The addition of

adsorbing oil was not considered to have caused a step change in the agglomerate surface properties at low oil levels since problems such as incomplete wetting and surface roughness [15] will contribute some coal character to the surface.

Neumann *et al.* [16,17,18] have developed an equation of state relating an interfacial tension to two known surface tensions. This is coupled with Young's Equation to determine the system.

Neumann's surface tension equation of state is,

$$\gamma_{SL} = \frac{(\sqrt{\gamma_{SV}} - \sqrt{\gamma_{LV}})^2}{1 - 0.15\sqrt{\gamma_{SV}\gamma_{LV}}} \quad (1)$$

and Young's equation,

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \theta \quad (2)$$

Equation 1 gives interfacial tensions for the coal, oil and water system at each agglomerate oil level. Now using equation 2, the three-phase contact angle can be calculated. In Figure 4, the three-phase contact angle is plotted against the agglomerate oil level.

4.2 Calculation of Bond Volumes

It has been shown that bonding structure of agglomerates is determined by the volume ratio of binding liquid to solid present in the system. At the binder levels considered in this work, the bonding should be exclusively pendular. [19,20] Pendular bonds are discrete lens-shaped rings at the point of contact of two particles. With different three-phase contact angles at the different oil levels, the oil bond profile will vary. If the effect of gravity is neglected, the binder-liquid interface will assume a profile of constant curvature and thus can be represented by an arc of a circle of radius b . (Figure 4, inset)

The meridian angle, θ_m can have a maximum size of 45° in the pendular regime, or else neighbouring bonds will coalesce. Now assume the particle has a unit radius, defined by the equation $x^2 + (y-1)^2 = 1$. With θ_m equal to 45° , the three-phase junction will occur at the point $x = 1/\sqrt{2}$, $y = 1 - 1/\sqrt{2}$.

The meniscus surface can be defined by an arc of a circle defined as,

$$(x-a)^2 + y^2 = b^2 \quad (3)$$

Equation 3 along with the particle profile and θ_C determine the parameters a and b . Thus for a given contact angle, the meniscus profile is defined.

The absolute bond volume, V_{BA} , can be then taken as a volume of revolution of the meniscus area. Let the meniscus surface be $\mathcal{F}_2(y)$ and the particle surface be $\mathcal{F}_1(y)$. y_c is the three-phase contact point y -coordinate.

$$V_{BA} = 2\pi \int_0^{y_c} [\mathcal{F}_2(y)]^2 dy - 2\pi \int_0^{y_c} [\mathcal{F}_1(y)]^2 dy \quad (4)$$

Equation 4 was integrated numerically with a 15-point Gaussian quadrature routine. The bond volume as a function of contact angle is plotted in Figure 4. Newitt and Conway-Jones [20] define the bond volume as a function of meridian angle θ as,

$$V_{BA} = 2\pi r^2 (\sec \theta - 1)^2 \left[1 - \left(\frac{\pi}{2} - \theta \right) \tan \theta \right] \quad (5)$$

The V_{BA} calculated for $\theta_C = 0^\circ$ is exactly the same result as predicted by equation 5. Define V_{OB} as the ratio of V_{BA} to the volume of two particles.

4.3 Interdependence of the Surface Tension, Oil Level and Enlargement Factor

An informative way of expressing agglomeration data is with an enlargement factor, F . F can be defined as,

$$F = \frac{d_p}{d_{p_0}} \quad (6)$$

where d_p is a mean agglomerate diameter at a given oil level and d_{p_0} is the mean diameter of the unagglomerated coal.

Figure 5 shows F plotted against oil level.

Assume that at low oil levels, only single particles and doublets will contribute to the resulting enlargement factor. Now say that there are n particles and one of them is double size (an agglomerate). Thus,

$$F - 1 = \frac{1}{n} \quad \text{or,} \quad n = \frac{1}{F - 1} \quad (7)$$

One bond will exist for every $n + 1$ individual particles, so the fraction of the total solid volume that is bonded in doublets, V_{SB} , is,

$$V_{SB} = \frac{2}{n + 1} \quad (8)$$

Thus the bonding volume of oil, V_{OB} , relative to the volume of the two bonded particles is,

$$V_{OB} = \frac{V_O(n + 1)}{2} \quad (9)$$

where V_O is the total volume of oil expressed as a fraction of the total solids volume. However, for a given volume of solids, the oil will first be consumed in wetting the solid surface, then any excess will be used up in forming bonds. The total oil volume, V_O , will be composed of two parts, a bonding volume, V_B , and a wetting volume V_W . Thus, V_B is substituted for V_O in equation 9 to account for the wetting volume.

It is of interest to determine how the oil distributes itself to bring about the observed agglomeration results.

Recall equation 9. Since $1/n = F - 1$, it may be re-expressed as,

$$V_{OB} = \frac{V_B F}{2(F - 1)} \quad (10)$$

Assume that at low oil levels only pendular bonds will exist. Thus the volume of one bond V_{OB} , is known and can be used to calculate V_B and V_W . Assuming V_W is constant for all oil levels, equation 10 may be used to determine the bond volume per particle pair.

Denote V_{OB} from equation 10 as real volume V_R , and V_T as the theoretical volume. The ratio V_R/V_T will give a mean value of bonds per particle. If $V_R/V_T > 1$, then this implies that agglomerates larger than doublets exist. Figure 5 shows this ratio plotted versus oil level. One may note the similarity between Figures 5 and 2. At an oil level of about 1 to 2 weight%, the slopes on these plots significantly change. The underlying reason for this change should be a fundamental change in the agglomerate structure. Based on the size data and the surface approximating that of hexadecane, it appears that beyond 2 weight% oil, larger, more compact agglomerates are formed.

A number of factors constrain the system. The result must conform to a mass balance of solids, an oil balance, and a weighted sum of various agglomerate sizes that accounts for the observed size. A system of three linear equations may be written which determine the distribution of singlets, doublets and triplets at each oil level based on the above criteria. They may be expressed as follows,

$$\begin{aligned} a_{11}q_1 + a_{12}q_2 + a_{13}q_3 &= F \\ a_{21}q_1 + a_{22}q_2 + a_{23}q_3 &= 1 \\ a_{31}q_1 + a_{32}q_2 + a_{33}q_3 &= V_B \end{aligned} \quad (11)$$

where the q_i 's are the fraction of singlets, doublets and triplets, the a_{1i} 's are the mean size of each type of agglomerate, the a_{2i} 's are all equal to 1 by mass balance and the a_{3i} 's are the bond volumes per agglomerate based on the oil level.

This system of equations was solved and it gave positive element solution vectors up to 2 weight% oil. At that point, the number of doublets predicted was negative (physically impossible) thereby indicating agglomerates larger than doublets are present which require substantially more oil due to the increased number of bonds per agglomerate.

The system was remodeled to include four-particle agglomerates that were considered to be in tetrahedral form having six bonds. This required an additional linear equation, and one was formulated based on the strength of the agglomerates. Consider each agglomerate in terms of the probability that it will break up, P_b . In general P_b should be proportional to the inverse of the number of bonds present. That is,

$$P_b \propto \frac{1}{nb}$$

where n is the number of bonds in the agglomerate and b is the bond strength. The probability of break-up of the singlet may be expressed as k_0b , where k_0 is some unknown constant. Thus for singlets through quadruples we have,

$$P_b = k_0q_1b + \frac{q_2}{b} + \frac{q_3}{3b} + \frac{q_4}{6b} \quad (12)$$

The strongest system, or minimum probability of break-up will occur when,

$$\frac{\partial P_b}{\partial b} = k_0q_1 - \frac{q_2}{b^2} - \frac{q_3}{3b^2} - \frac{q_4}{6b^2} = 0 \quad (13)$$

Rewriting equation 13 we obtain,

$$k_0b^2q_1 - q_2 - \frac{q_3}{3} - \frac{q_4}{6} = 0 \quad (14)$$

In this form, the coefficient a_{41} of the new 4×4 matrix is indeterminate. However, in view of the agglomerate data, it can be assumed that at 1 weight% oil, the solution element q_4 will be zero and a_{41} can be calculated from the 3×3 system results. The 4×4 system was then solved and gave positive solution element vectors from 1 weight% through 10 weight% oil. Interestingly, the 4×4 system predicts essentially the same distribution of sizes at 2 weight% oil as does the 3×3 system, indicating that the omission of quadruples from the model at very low oil levels is justified.

Figure 6 is a plot of the frequency of each agglomerate size versus oil level as calculated by the system of linear equations. It can be seen from Figure 6 that the frequency of singlets as a function of oil level is a smooth curve supporting the above assumptions.

The above development was also calculated with the assumption of a zero contact angle at the three-phase interface, as assumed in previous papers. [21,22] The results predicted overly large particles at low oil levels as the zero contact angle bond is about half the volume of the finite contact angle bond. Correspondingly the wetting volume with a zero contact angle was found to be much larger as well.

5 Conclusions

The adhesion surface tension method and a laser diffraction particle sizer provided means of measuring respectively the surface tension and particle-size distributions of agglomerates formed from metallurgical coal and *n*-hexadecane in an aqueous suspension of the agglomerates.

From this study it can be said that the amount of oil introduced to a coal-water slurry for forming agglomerates determines several properties on the agglomerate surface. The net agglomerate surface tension was found to approach that of the pure oil at increased oil levels, and as such the three-phase contact

angle between the agglomerate, the oil meniscus and the suspending water decreased. Thus at oil levels below 2 weight%, the bond volumes were great enough to consume the available oil in forming agglomerates no larger than doublets and triplets. With smaller contact angles at higher oil levels, the particle bonding is more economical and larger more compact oil-wetted agglomerates are seen. A constraining system of linear equations was developed to illustrate this.

A more complete analysis would involve a statistical approach encompassing the entire particle-size distribution instead of the mean particle size used here.

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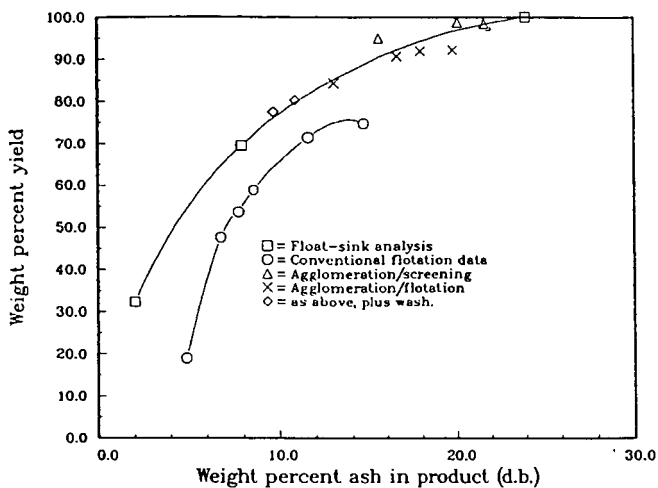


Figure 1: Yield-ash results for a minus 28 run of mine coal from Pennsylvania. (Wt.% reagent levels are based on feed solids).

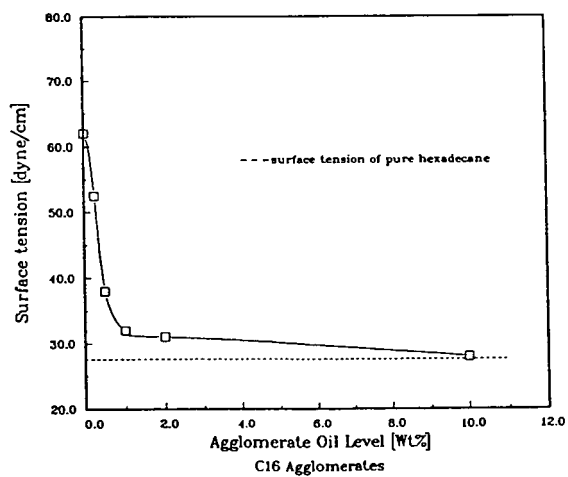


Figure 2: Agglomerate Surface Tension vs. Oil Level

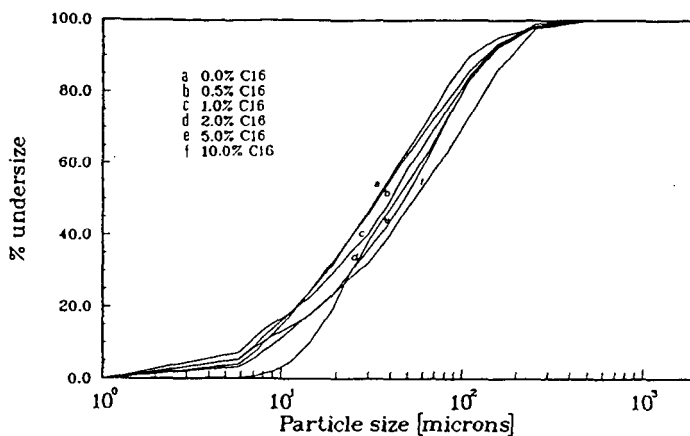


Figure 3: Particle-size distributions of agglomerates for $n\text{-C}_{16}\text{H}_{34}$ levels from 0 to 10 weight%

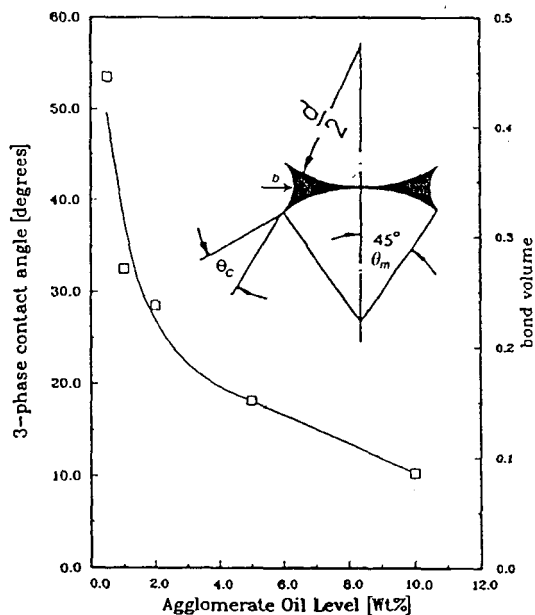


Figure 4: θ_C and V_{BA} vs. Oil Level.
- inset is schematic of 3-phase contact angle in particle-bonding context

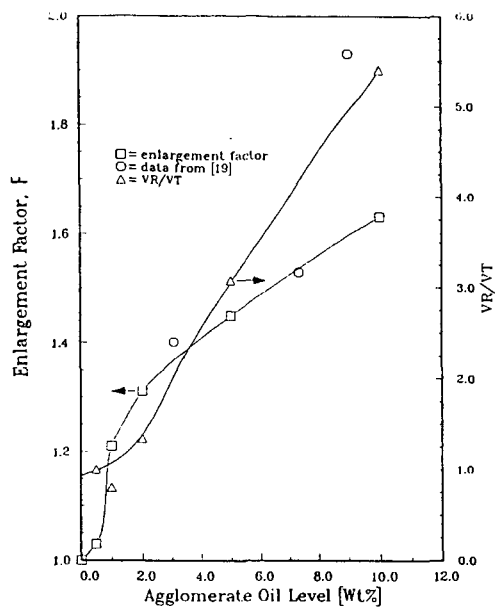


Figure 5: Enlargement Factor and V_R/V_T vs. Oil Level

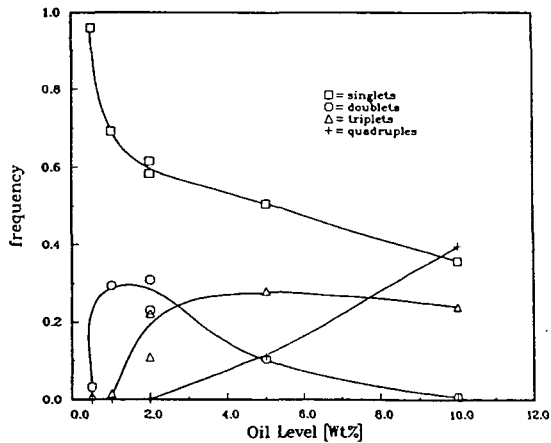


Figure 6: Agglomerate Size Frequency vs. Oil Level